

PATENT ABSTRACTS OF JAPAN

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(54) POLYESTER CHIP

(57)Abstract:

PURPOSE: To provide polyester chips manufactured by solid-state polymn., exhibiting a homogeneous flowability during melt molding, and suitable as the material of a tire cord (fiber), a bottle, etc.

CONSTITUTION: Homogeneity during melt molding and stabilization of (improvement in) moldability of polyester chips prepd. by the solid-state polymn. of a prepolymer are achieved by keeping the differences in intrinsic viscosity and density between the outer layer and inner part of each chip to 0.125 or lower and 0.0019 or lower, respectively. The differences appear when the intrinsic viscosity of the prepolymer is raised by at least 0.15 in the solid-state polymn.

LEGAL STATUS

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About a polyester solid-state-polymerization chip, in melting shaping of extrusion molding, such as fiber, a film, or a bottle, injection molding, etc., this invention is fused easily and relates to the polyester chip which is equal to especially high velocity forming and by which solid state polymerization was carried out.

[0002]

[Description of the Prior Art] Mechanical, physical, and since it excels in chemical property, polyester is widely used in fiber, a film, a bottle, industrial resin, etc.

[0003] In order to low-carboxylate among these in the field of which the resistance to moist heat of a tire cord, dryer canvas, etc. is required Moreover, in order to form high intrinsic viscosity in the field of which high strength, such as sewing thread and a tire cord, is required In order to low-oligomerize in the field of which low Society for Cutting Up Men in the film for electric insulation etc. and a production process is required Generally in the field in which tastes and smells, such as a carbonic acid bevel-use bottle, are made into a problem, performing [many] solid state polymerization for the various purposes, in order to form a low acetaldehyde are

made. However, in heating from the outside raising polymer temperature, since a reaction advances by spreading outside low molecular weight compounds generated as a result of a reaction, such as water and a glycol, and removing them from a front face outside, in one chip, a quality difference surely produces solid state polymerization in the inner layer (nucleus part) and outer layer (the near front face) of the chip. For example, the outer layer of intrinsic viscosity is higher, and probably because the heat of crystallization accumulates a consistency in the interior, it is higher [the interior].

[0004] When carrying out melting shaping on condition that usual, it does not become especially a problem, but if the ***** shaping rate which raises productivity is raised at the time of shaping, the difference of the melting behavior by the inner outer layer difference of this chip will come to affect a moldability and mold-goods physical properties gradually.

[0005] Although melting temperature is raised, or the heating hopper is provided so that the chip temperature before going into a making machine in order to prevent this may become high, since the polymer is melted forcibly, a part of polymer understands, or mold-goods quality becomes an ununiformity, and a limitation is in productivity.

[0006]

[Problem(s) to be Solved by the Invention] This invention makes it the technical problem of invention to offer a polymer chip with which the quality of a moldability or mold goods does not deteriorate even if it carries out high-speed melting shaping and which is easy to fuse.

[0007]

[Means for Solving the Problem] this invention -- a solid-state-polymerization method -- the intrinsic viscosity -- at least 0.15 -- in the polyester chip made high, it is the solid-state-polymerization chip of the polyester which makes it requirements for the intrinsic-viscosity difference of an outer layer and a inner layer to be 0.125 or less, and for the consistency difference to be 0.0019 or less.

[0008] In this invention, "polyester" means the polyester which uses aromatic series dicarboxylic acid as a main acid component, and uses an aliphatic series glycol as a main glycol component. here -- "-- being main -- " -- dicarboxylic acid and a glycol mean occupying more than 85 mol %. It is the technique in which this invention can apply the thing containing the 3rd component not more than 15 mol %.

[0009] As "aromatic series dicarboxylic acid" which constitutes polyester, a terephthalic acid, naphthalene dicarboxylic acid, diphenyl dicarboxylic acid, diphenyl ether dicarboxylic acid, diphenyl ketone dicarboxylic acid, difenoxycarboxylic acid, etc. can be illustrated.

[0010] As an "aliphatic series glycol" which constitutes polyester, ethylene glycol, a trimethylene glycol, tetramethylene glycol, hexamethylene glycol, etc. can be illustrated.

[0011] As the 3rd component which can be copolymerized, there are aromatic series dicarboxylic acid which constitutes the polyester, dicarboxylic acid other than an aliphatic series glycol, diol, and hydroxy acid. Specifically other than said compound,; aliphatic series dicarboxylic acid, for example, a malonic acid, such as; alicycle group dicarboxylic acid, for example, decalin dicarboxylic acid, such as aromatic series dicarboxylic acid, for example, isophthalic acid, diphenylsulfone dicarboxylic acid, diphenyl ketone dicarboxylic acid, sodium-sulfoisophtharate, and a dibromo terephthalic acid, tetralin dicarboxylic acid, and a hexahydro terephthalic acid, a succinic acid, an adipic acid, a sebacic acid, etc. are illustrated. As a glycol

component, moreover, aliphatic series diol, for example, pentamethylene glycol, A diethylene glycol, triethylene glycol, etc.; Aromatic series diol, For example, a catechol, naphthalene diol, resorcinol, 4, and 4'-dihydroxy-diphenyl-sulfone, Bisphenol A [a 2 and 2'-screw (4-hydroxyphenyl) propane], Tetrabromobisphenol A, bis-hydroxy ethoxy bisphenol A, etc.; Alicycle group diol, A metaphor; aliphatic series hydroxy acid, such as ** cyclohexane diol, For example, chestnut cholic acid, hydracrylic acid, a 3-oxy-propionic acid, etc.; Alicycle group hydroxy acid, For example, a reed ACHIN acid, a KINOBA acid, etc.; aromatic series hydroxy acid, for example, a salicylic acid, an m-oxy-benzoic acid, a p-oxy-benzoic acid, mandelic acid, atrolactic acid, etc. can be mentioned.

[0012] It is easy to be even if it will add a monofunctional compound, for example, o-benzoylbenzoic acid, a naphthoic acid, etc., if the multifunctional compound more than trivalent, for example, a glycerol, trimethylol propane, pentaerythritol, trimellitic acid, trimesic acid, pyromellitic acid, a TORIKARU valine acid, a gallic acid, etc. may be copolymerized and it requires for within the limits whose polyester is furthermore a line substantially.

[0013] Moreover, what contained a wear agent, a flame retarder, a fire-resistant assistant, an anti-oxidant, an ultraviolet ray absorbent, a pigment, a color, an easy lubricating agent, a crystallization nucleating additive, a crystallization accelerator, reinforcing materials, etc. if needed may be used.

[0014] The prepolymer before performing solid state polymerization of the polyester of this invention can usually be manufactured by the well-known approach. For example, after carrying out the ester exchange reaction of an approach, and the low-grade alkyl ester and the glycol of an acid which carry out melt polycondensation under existence of a suitable catalyst after esterifying an acid and a glycol directly under existence of a suitable catalyst, the approach of carrying out melt polycondensation etc. is mentioned. In any case, it cools with melting extrusion and a suitable catalyst, for example, underwater, after melt polycondensation, and cuts and chip-izes in suitable magnitude. Even when a chip is spherical also at the shape of a rectangular parallelepiped or the shape of a cylinder, and a die, it is good.

[0015] The polyester of this invention performs solid state polymerization until it makes intrinsic viscosity high 0.15 or more at the temperature below the melting point further and becomes a desired value about the polymer obtained in this way.

[0016] When the intrinsic-viscosity difference before and behind solid state polymerization is 0.15 or more, a difference with a conventional method becomes clear and the effectiveness becomes remarkable.

[0017] Under an inactive air current or a vacuum (under reduced pressure), and it can also apply continuous system or a batch process. [the solid state polymerization in this invention] Furthermore, a packed column type, a horizontal-type clinker type, or a tumbler type is sufficient.

[0018] In this invention, it is requirements that the intrinsic-viscosity difference of the outer layer of the chip after solid state polymerization and a inner layer is 0.125 or less, and the consistency difference is 0.0019 or less. In addition, they are 0.120 or less intrinsic-viscosity difference and 0.0018 or less consistency difference preferably.

[0019] In this invention, a "outer layer" means from the outside surface of a chip to 0.5mm inside. Moreover, a "inner layer" means from the core of a chip to 0.3mm outside. Cutting and collecting how many grains of outer layers from that chip in an outer layer, a inner layer is cut as a inner layer, are collected, and measure intrinsic viscosity and a consistency, respectively. Although it will be based also on a chip configuration or solid-state-polymerization conditions if solid state polymerization is

carried out by the usual approach, the intrinsic-viscosity difference of an inside-and-outside layer is large from 0.15, and 0.25 and a consistency difference are 0.0020 to 0.0030.

[0020] The following approaches are illustrated, in order to process the inner outer layer difference in the chip of intrinsic viscosity and a consistency so that it may become within the limits of this invention.

- (1) Make a chip configuration small. For example, it is made 2.8mm or less as a spherical equivalent diameter.
- (2) Make chip thickness thin, for example, in the case of the shape of a rectangular parallelepiped or a cylinder, set thickness or width of face to 1.8mm.
- (3) Keep solid-state-polymerization temperature low. For example, in the case of polyethylene terephthalate, it may be 215 degrees C or less.
- (4) Hold down the carrier gas flow rate used for solid-state-polymerization reaction time to 1 or less m/sec by superficial velocity.
- (5) At the crystallization process before solid state polymerization, increase a carrier gas flow rate conversely so that crystallization generation of heat may not carry out accumulation.
- (6) In performing solid state polymerization gradually, it maintains the first stage at low temperature as much as possible.
- (7) By microwave heating, the interior of a chip also carries out homogeneity heating. These need to combine two or more means, when the purpose cannot be attained by one approach.

[0021]

[Effect of the Invention] Even if the solid phase chip by this invention has a small inside-and-outside layer quality difference and carries out high-speed melting shaping, neither a melting ununiformity nor a flow ununiformity happens, but the stable moldability and mold-goods quality are acquired.

[0022]

[Example] Below according to an example, this invention is ****(ed). In addition, the "section" means the weight section among an example. Moreover, the measuring method of a property used in the example is shown below.

1) Intrinsic viscosity : $[\eta]$

It computed from the melt viscosity measured at 35 degrees C using the mixed solvent of a phenol/tetrachloroethane (weight ratios 60/40).

2) Consistency : the consistency in 25 degrees C was measured among density gradient tubing of n-heptane / carbon-tetrachloride system.

[0023] Using the cylinder-like polyethylene TEREFURETA rate chip of intrinsic-viscosity 0.55 dl/g shown in the example table 1 of polymer manufacture, solid state polymerization was performed on predetermined conditions using the continuous system model clinker type solid-state-polymerization facility, and the solid-state-polymerization chip which has various inside-and-outside layer quality differences was obtained.

[0024] As for the thing of a type, the thing to which both the polymers C are suitable for high velocity forming included in this invention range, and Polymers B and D, in Polymer A, either separates from this invention range conventionally which also separated the intrinsic-viscosity difference and consistency difference from the range of this invention.

[0025]

[Table 1]

[Table 1]

ポリマ マー	アレポリマー			固相重合		チップ品質			
	チップ 形状	厚さ×巾×長さ mm	[η] dl/g	方 式	温度 ℃	[η]		密 度	
						内 層	外 層	内 層	外 層
A	シリンダ ー状	2.0×4.0×3.5	0.55	連続式模塑クリン カータイプ	228	0.813 (差 0.191)	0.804 (差 0.0027)	1.4089 (差 0.0027)	1.4062 (差 0.0027)
B	"	1.7×4.0×4.0	"	"	"	0.622 (差 0.169)	0.791 (差 0.0019)	1.4061 (差 0.0019)	1.4042 (差 0.0019)
C	"	"	"	"	214	0.670 (差 0.117)	0.787 (差 0.0018)	1.4057 (差 0.0018)	1.4039 (差 0.0018)
D	"	1.9×4.0×3.5	"	"	"	0.652 (差 0.123)	0.775 (差 0.0022)	1.4061 (差 0.0022)	1.4039 (差 0.0022)

[0026]

[Example 1] A part for 50g/in regurgitation rate performed spinning at 290 degrees C of cylinder temperatures using the extruder of the diameter of 30mm using Polymers A, B, C, and D. When raised the screen rotational frequency next since neither is problematic and 4-hour spinning was carried out, and it scraped off by part for 75g/in regurgitation rate, the rate was also raised 1.5 times and spinning was performed, Polymers A and B had the large throat pressure fluctuation, and A carried out the thread breakage of the 1st hour and the B in the 2nd [about] hour. Although C and D have been spun in the state of unapproved yarn for 4 hours, the yarn from the polymer of D had large denier spots.

[0027]

[Example 2] The injection molding machine with the screw of the diameter of 105mm performed bottle shaping using the preforming metal mold of 48-piece picking using Polymers A, B, C, and D. It started in the 40-second cycle (a part for 72/) at first, and shaping speed was raised for every hour. When Polymer A became a 33-second cycle (a part for 87/), the flow pattern appeared charge fluctuation in a lifting and the regio oralis of preforming. When it became a 30-second cycle (a part for 96/), the same phenomenon came out of Polymer B. Polymers C and D are normal to a 27-second cycle (a part for 107/), and it has stabilized and fabricated. However, preforming which consists of a polymer D started HIKE to the part, when crystallizing the regio oralis.

[Translation done.]